

# Persistent insulating behavior in 5d transition metal oxides $\text{Sr}_2\text{IrO}_4$ and $\text{Sr}_3\text{Ir}_2\text{O}_7$ at high pressures

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## Abstract

Iridium-based 5d transition-metal oxides are attractive candidates for the study of novel correlated electronic states due to the enhanced crystal-field and spin-orbit interaction energies. We present electrical resistivity  $\rho(T)$  measurements up to pressures in excess of 100 GPa performed on single crystals of  $\text{Sr}_2\text{IrO}_4$  and  $\text{Sr}_3\text{Ir}_2\text{O}_7$ , which at ambient pressure display an unexpected  $J_{\text{eff}} = 1/2$  Mott-insulating state, characterized by a gap of the order of  $\sim 0.1$  eV. Our results show no indication of a pressure-induced metallic state up to 55 GPa in  $\text{Sr}_2\text{IrO}_4$  and to 104 GPa in  $\text{Sr}_3\text{Ir}_2\text{O}_7$ . The resistivity of  $\text{Sr}_3\text{Ir}_2\text{O}_7$ , measured at 10 K, decreases by more than five orders of magnitude between ambient pressure and 104 GPa, suggesting the proximity of this compound to a metal-insulator transition.

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## A. INTRODUCTION

Metal-to-insulator transitions (MIT) have been widely studied in transition-metal oxides (TMOs), mainly motivated by the discoveries of high-temperature superconductivity in cuprates and colossal magnetoresistance in manganites.[1] As opposed to the Mott-insulating ground state found in the 3*d*-electron compound  $\text{La}_2\text{CuO}_4$ , a metallic ground state is expected to be found in iridium-based TMOs, due to the highly delocalized 5*d* electronic orbitals of the Ir ions. However, non-metallic behavior has been found in  $\text{Sr}_2\text{IrO}_4$  (214) and  $\text{Sr}_3\text{Ir}_2\text{O}_7$ (327), which are members of the Ruddelsden-Popper series  $\text{Sr}_{n+1}\text{Ir}_n\text{O}_{3n+1}$  ( $n$  = number of  $\text{IrO}_2$  layers). The unexpected insulating behavior has been attributed to the strong spin-orbit coupling (SOC = 0.2-1 eV) which in these compounds is comparable to the Coulomb repulsion  $U = 0.5 - 2$  eV (SOC  $\sim 0.01$  eV in 3*d* TMOs), giving rise to an unexpected  $J_{\text{eff}} = 1/2$  Mott-insulating ground state.[2] With increasing  $n$ , the bandwidth  $W$  associated with the 5*d* orbitals increases and the Mott gap becomes smaller, from  $\sim 0.1$  eV for the 214 compound to a gap value almost equal to zero for the 327 material, and with a metallic state recovered in the  $n = \infty$  compound, namely  $\text{SrIrO}_3$  (Ref. 3).

$\text{Sr}_2\text{IrO}_4$  forms in a reduced tetragonal  $I4_1/acd$  structure, similar to the tetragonal  $I4/mmm$  but with the  $\text{IrO}_6$  octahedra rotated by  $11^\circ$  about the  $c$ -axis, which increases the size of the unit cell.[4, 5] It orders into a antiferromagnetic (AFM) state below  $T_N = 240$  K, with canted Ir moments in the  $ab$ -planes.[6, 7] On the other hand, the structure of  $\text{Sr}_3\text{Ir}_2\text{O}_7$  is still under debate, although recent experiments suggest that a tetragonal  $I4/mmm$  structure would be reasonable, given the fact that the rotation of the  $\text{IrO}_6$  octahedra does not seem to be correlated as in the case of  $\text{Sr}_2\text{IrO}_4$ , due to the lack of additional reflections in the X-ray patterns.[8] The bilayer  $\text{Sr}_3\text{Ir}_2\text{O}_7$  displays long range AFM order below  $T_N = 285$  K, with  $c$ -axis collinear moments.[9] It has recently been pointed out that the Ir-O-Ir bond angle controls the electronic hopping and the magnetic interaction between the Ir atoms, which allows the physical properties to be tuned via chemical doping[10] or substitution,[11] or with the application of magnetic field[12] or pressure.[13]

In this paper, we report measurements of the electrical resistivity  $\rho(T)$  of  $\text{Sr}_2\text{IrO}_4$  and  $\text{Sr}_3\text{Ir}_2\text{O}_7$  single crystals as a function of temperature under high pressure. These experiments were motivated by the small values of the Mott-insulating gap in these compounds which one could expect to quench with externally applied pressure. Contrary to the recent metallic

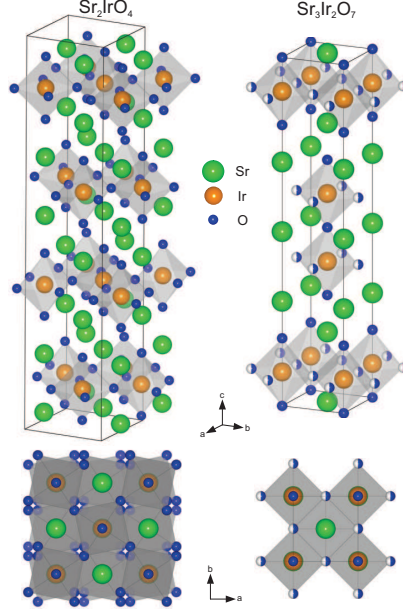


FIG. 1: Crystal structure of single-layer  $\text{Sr}_2\text{IrO}_4$  and double-layer  $\text{Sr}_3\text{Ir}_2\text{O}_7$ . The O and Ir atoms form octahedra, which are rotated by  $11^\circ$  about the  $c$ -axis in  $\text{Sr}_2\text{IrO}_4$ . An undistorted  $I4/mmm$  tetragonal structure is shown for  $\text{Sr}_3\text{Ir}_2\text{O}_7$ , since no additional X-ray diffraction peaks associated with the  $\text{IrO}_6$  rotation has been observed in this compound.

state induced by chemical substitution in the 214 compound,[11] we find no signs of a pressure-induced metallic state in  $\text{Sr}_2\text{IrO}_4$  and in  $\text{Sr}_3\text{Ir}_2\text{O}_7$  up to maximum applied pressures of 55 GPa and 104 GPa, respectively.

## B. EXPERIMENTAL DETAILS

Single crystals of  $\text{Sr}_2\text{IrO}_4$  and  $\text{Sr}_3\text{Ir}_2\text{O}_7$  were grown by means of a molten metal flux method as described in Ref. 7. Measurements of  $\rho(T)$  along the  $ab$  crystallographic plane were performed for  $1\text{ K} \leq T \leq 300\text{ K}$  under nearly-hydrostatic pressure conditions up to 2.3 GPa employing a Be-Cu piston-cylinder hydrostatic cell (HC), using a 1:1 mixture by volume of  $n$ -pentane and isoamyl alcohol as the pressure transmitting medium and a Teflon capsule. Electrical contacts were made by attaching with conducting epoxy four  $50\text{ }\mu\text{m}$  Pt wires to the surface of the crystals. Pressure was determined by measuring the superconductivity of a Sn manometer.[15] An initial pressure of 0.1 GPa was needed to clamp the cell and prevented the fluid pressure medium to flow away from the device.

For higher pressures, a Bridgman-anvil cell (BAC) and a diamond-anvil cell (DAC) were used. In the BAC, two opposite WC anvils (4 mm diameter anvil flats) compressed the sample and the manometer, located in between two disks of 2 mm in diameter made of pressed steatite powder, which has a low shear-stress coefficient and served as a quasi-hydrostatic pressure medium. The gasket was composed of a pyrophyllite ring of 0.25 mm of thickness. Electrical contacts were obtained by laying down onto the sample four 50  $\mu\text{m}$  Pt wires with flattened tips, which reached the sample chamber through grooves cut in the pyrophyllite ring. Pressure was determined by measuring the superconducting transition of a Pb manometer.[16] The DAC employed in the experiments reported herein is a mechanically loaded model, manufactured by Kyowa Seisakusho Ltd.. The upper anvil consists of a non-beveled blank diamond, with a tip of 300  $\mu\text{m}$  in diameter, while the diamond used at the bottom is called “designer” diamond (DD),[17] since it contains eight deposited tungsten microprobes encapsulated in high-quality homoepitaxial diamond, for  $\rho(T)$  measurements. The DD have a culet size of 500  $\mu\text{m}$  and beveled to a tip of 250  $\mu\text{m}$ . The gasket was made from a 200  $\mu\text{m}$  thick MP35N foil pre-indented to 50  $\mu\text{m}$ , and a 100  $\mu\text{m}$  diameter hole was drilled through the center of the indentation using an electrical discharge machine. The sample space corresponds to the volume enclosed by the hole in the gasket and the flat tips of the two diamonds, and for these experiments, the sample was packed in this cavity, without pressure medium to obtain electrical contact with the DD. For the BAC and DAC, electrical contacts were obtained by pushing the leads against the sample during pressurization, and a minimum pressure of 2-3 GPa was necessary to obtain low contact resistance.

Pressure gradients were inferred from the width of the superconducting transition of the manometer for the HC ( $\delta P < 2\%$ ) and the BAC ( $2\% < \delta P < 10\%$ ). For the DAC, the pressure was adjusted at room temperature, using the fluorescence spectrum of chips of ruby located within the sample chamber, with a  $\delta P \leq 15\%$ , inferred from the full width at half maximum (FWHM) of the fluorescence line. Pressure gradients in the sample chamber were inferred from the pressure difference between different rubies. In all cases, the electrical resistance was measured with a Linear Research Inc. LR-700 AC resistance bridge (maximum resistance = 2 M $\Omega$ ) using a standard four-lead technique.

### C. $\text{Sr}_2\text{IrO}_4$

The electrical resistivity  $\rho$  (logarithmic scale) versus temperature  $T$  of  $\text{Sr}_2\text{IrO}_4$  is displayed in Fig. 2, measured in the HC and BAC.  $\rho(T)$  increases by more than five orders of magnitude while cooling from 300 K to 1 K. No anomaly at  $T_N \sim 240$  K was observed, similarly to previous reports.[12] The data obtained in the HC can be described using various models in different regions of the temperature scale, as previously reported for polycrystalline[18] and single-crystalline samples:[11]

1) From 150 K to 300 K, our data fit best to an expression appropriate for a weakly-localized two-dimensional system, with  $\log(\rho) \propto -T$ , which can be attributed to the effects of structural disorder present in the material.[18]

2) From 50 K to 125 K, the  $\rho(T)$  data exhibit activated behavior, and can be described by an exponential function  $\rho(T) = A \exp(\Delta/2k_B T)$ , where  $\Delta$  is the energy gap,  $A$  is a constant and  $k_B$  is the Boltzmann constant.  $\Delta$  was estimated by plotting  $\ln \rho(T)$  versus  $1/T$  and fitting a straight line to the data (Fig. 3). The inset of Fig. 3 displays the values of  $\Delta$  vs.  $P$ , and includes data from the measurements made in the DAC (Fig. 4). For the HC measurements, the slopes of the curves are practically equal, resulting in values of  $\Delta$  of  $80 \text{ meV} \pm 5 \text{ meV}$ , similar to the ambient pressure value previously reported, from which one can mainly conclude that a pressure of the order of 2 GPa does not affect substantially the energy gap. The slopes corresponding to the BAC change more noticeably from 2.1 GPa to 16 GPa, resulting in an initial increase of  $\Delta$  up to a value of 100 meV at 7.4 GPa, followed by a single data point with a lower value of  $\Delta \sim 90 \text{ meV}$  at 16 GPa. The  $\rho(T)$  curves obtained in the DAC (Fig. 4) deviate considerably from the Arrhenius form in the selected temperature range, most probably due to the large pressure gradients present in the sample chamber at these extreme conditions. Keeping in mind the large error involved in these fits, it is still possible to observe that the values of energy gap obtained from the DAC experiment decrease with pressure, consistently with the behavior obtained in the BAC experiment above 10 GPa.

Overall, our data is in sharp contrast to previous high-pressure experiments,[13] where a monotonic decrease of  $\Delta(P)$  from 60 meV at 1 GPa to 30 meV at 30 GPa was found. In both cases, the samples were pressurized under very different conditions of hydrostaticity: a soft powder was utilized as pressure transmitting medium in the previously reported ex-

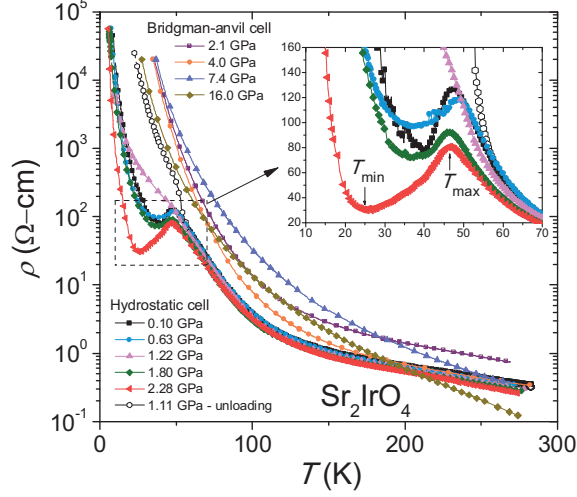


FIG. 2:  $\rho$  vs.  $T$  of  $\text{Sr}_2\text{IrO}_4$  measured in the hydrostatic cell (HC) and the Bridgman-anvil cell (BAC) experiments.  $T_{\max}$  and  $T_{\min}$  indicate a possibly additional magnetic transition previously reported.[12]

periments and the electrical resistance was presumably measured along the  $ab$  plane of one single crystal, while three different pressure techniques were utilized in our experiments (a hydrostatic HC, a quasi-hydrostatic BAC, and a very non-hydrostatic DAC configuration). The remarkable difference between data sets persists even if we limit our conclusions to our most hydrostatic data measured below 10 GPa, from which it is clear that  $\Delta$  increases with pressure. Unfortunately, we cannot draw any conclusion regarding the quality of the fits from which the data in Ref. 13 was determined. Taking into account the highly anisotropic transport properties of  $\text{Sr}_2\text{IrO}_4$  (Ref. 12) and the important role played by the Ir-O-Ir bonding angle in determining the physical properties of the Ir-based TMOs,[19] the disparity of these results could presumably be explained as the effect of different uniaxial pressure dependences of the transport properties corresponding to the samples measured in each experiment. In order to shed light into these contrasting results, high-pressure experiments with a single technique, using He as the best hydrostatic pressure medium, would be desirable. Finally, and taking into account the high inaccuracy involved in the calculation of  $\Delta$  values from fits to  $\rho(T)$  plotted in the Arrhenius form, it would be necessary a more precise determination of  $\Delta(P)$  by means of optical spectroscopy.[20]

A sharp decrease of  $\rho(T)$  occurs in the HC measurements upon cooling below 50 K, followed by the reappearance of the insulating behavior below  $\sim 25$  K (inset of Fig. 2).[21] The

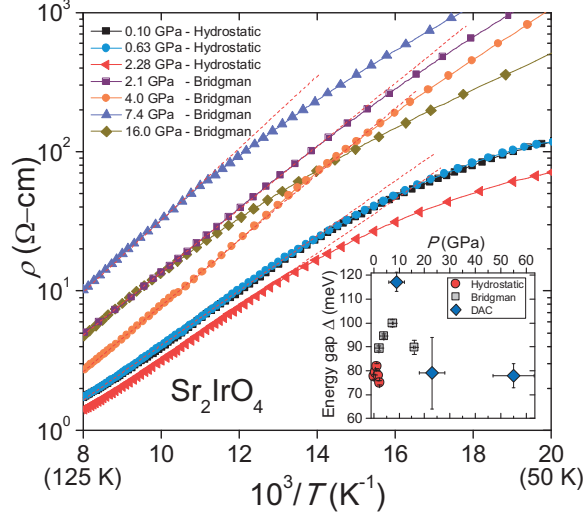


FIG. 3:  $\rho$  vs  $1/T$  for  $\text{Sr}_2\text{IrO}_4$  from the HC and BAC experiments. The linear fits in the selected temperature ranges yield values of the energy gap  $\Delta$  displayed in the inset.

onsets to these *s*-shaped features, denoted as  $T_{max}$ , remain practically unchanged throughout the whole pressure range. At 2.28 GPa, the highest value of pressure attained in the HC, the separation between  $T_{min}$  and  $T_{max}$  reaches a maximum. The *s*-shaped anomaly is surprisingly absent in the 1.22 GPa curve, and emerges again at 1.8 GPa. The absence of the sharp decrease of  $\rho(T)$  in the vicinity of 50 K was later confirmed upon decreasing the pressure to 1.11 GPa by unloading the clamp from 2.28 GPa. Although the pressure medium remains hydrostatic in all the pressure range of the HC experiment, it is still not trivial to tune the pressure in the sample during the unloading process, since the HC is a mechanical clamp and strong friction exists between the pistons and the cylinder. In this context, the pressure of 1.11 GPa was our best attempt to return the sample to a similar pressure state as in the 1.22 GPa, for which the *s*-shaped feature was absent in  $\rho(T)$ . Even though the 1.11 GPa measurement does not show the anomaly, the shape of the curve below 50 K is somehow different from the flat shape of the 1.22 GPa measurement. One possibility to explain this effect is that there is a smooth variation from the *s*-shaped state to the state with no anomaly, and that the 1.11 GPa falls somewhere in between. Experiments using a gas-membrane-driven high-pressure cell would allow to apply smaller pressure steps, from which hysteretic effects could also be studied in more detail.

The origin of the *s*-shaped anomaly remains unclear. A similar feature has been observed below 100 K in ambient pressure  $\rho(T)$  and magnetization,[10–12] and it has been suggested

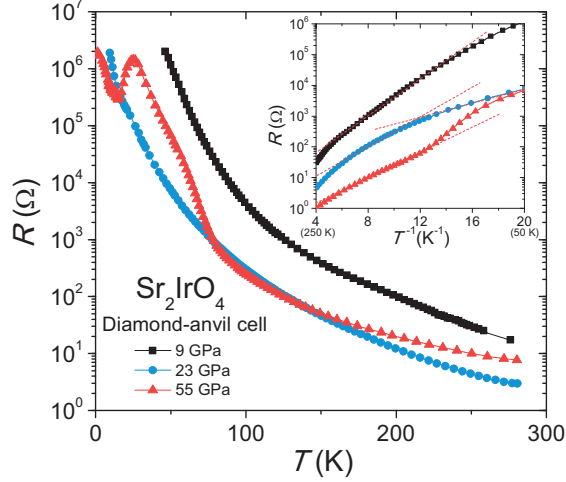


FIG. 4:  $\rho$  vs.  $T$  of  $\text{Sr}_2\text{IrO}_4$  measured in the diamond-anvil cell (DAC). Values of the energy gap  $\Delta$  shown in the previous figure were obtained from the fit to the data displayed in the inset.

that this abrupt deviation from the insulating behavior could originate from gradual canting of the Ir magnetic moments due to the  $T$ -dependent rotation of the  $\text{IrO}_6$  octahedra about the  $c$ -axis,[4] supported by the strong  $T$ -dependence of the bending phonon modes associated with the Ir-O-Ir bond angle observed in recent optical spectroscopy experiments.[19]

Fig. 4 displays the electrical resistance  $R$  of  $\text{Sr}_2\text{IrO}_4$  as a function of temperature corresponding to the diamond-anvil cell experiment.[22] There is a marked decrease of the overall resistance from 9 GPa to 23 GPa, while  $R(T)$  at 55 GPa displays a flattened curvature from room temperature to  $\sim 80$  K, followed by a sharper increase of  $R(T)$ , which could be related to the suppression of  $T_N$  to lower temperatures, as it is expected at these values of pressure.[13] Also at 55 GPa, an anomaly appears at 25 K very close to the resistance limit of our instrument; for this reason, we decided to disregard this portion of the measurement. The relative increase in the room-temperature sample resistance at 55 GPa compared to that at 23 GPa could possibly be due to the reduction of the thickness of the sample at high pressures. It is clear from the inset of Fig. 4 that these measurements deviate considerably from the Arrhenius form, which impeded us from performing an accurate energy gap analysis, as we have already discussed above.

At ambient pressure, the energy gap of  $\text{Sr}_2\text{IrO}_4$  ( $\sim 100$  meV) is considerably smaller than the value of the splitting of the  $J_{\text{eff}} = 1/2$  and  $J_{\text{eff}} = 3/2$  energy levels ( $\sim 500$  meV) due to the strong SOC. Recently, Haskell *et al.* suggested that a possible metallic state could

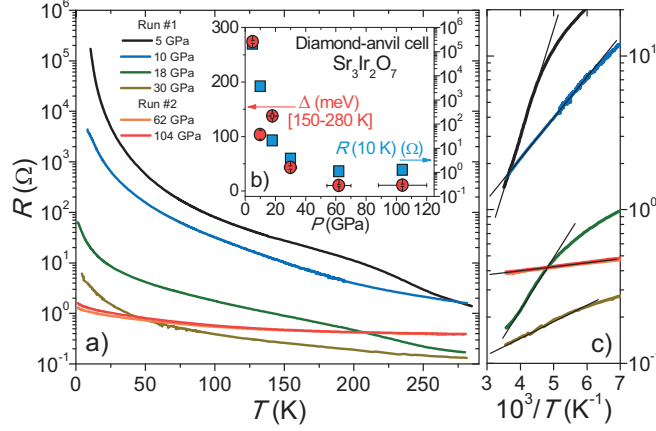


FIG. 5: a)  $R$  vs.  $T$  of  $\text{Sr}_3\text{Ir}_2\text{O}_7$  measured in two diamond-anvil cell runs. b) Values of  $R$  measured at 10 K (squares, right axis) and the energy gap values  $\Delta$  (circles, left axis) as a function of pressure, obtained from the fits to the data displayed in the c) panel.

appear above 100 GPa, after finding that the expectation value of  $\langle \mathbf{L} \cdot \mathbf{S} \rangle$  would vanish at an extrapolated pressure of 80-90 GPa.[13] Our diamond-anvil cell data presented in Fig. 4 show that  $\text{Sr}_2\text{IrO}_4$  remains non-metallic up to 55 GPa, suggesting that higher pressures are necessary to drive the system to a metallic state.

#### D. $\text{Sr}_3\text{Ir}_2\text{O}_7$

Figure 5a displays the electrical resistance  $R$  (logarithmic scale) of  $\text{Sr}_3\text{Ir}_2\text{O}_7$  obtained in the DAC. In the first run, a maximum pressure of 30 GPa was attained, while measurements of  $R(T)$  at 62 GPa and 104 GPa were made during a second DAC run. A hump below room temperature develops in the 5 GPa curve and is possibly related to the onset of the magnetic order.[23] This feature is absent at higher pressures, probably due to the strong pressure gradients along the sample which tend to soften the anomalies observed in electrical resistivity. The values of  $R$  at 10 K as a function of applied pressure are plotted in Fig. 5b (right axis), showing a dramatic reduction by more than five orders of magnitude. The curves at 62 and 104 GPa are quite similar, with  $R$  being almost temperature independent. Under these extreme conditions, large pressure gradients develop in the sample, which are reflected in the large error bars associated with the values of pressure determined from different ruby spheres located in the sample chamber. The values of the Mott energy gap  $\Delta$  can also be determined as in the  $\text{Sr}_2\text{IrO}_4$  case described above, and are plotted versus

pressure also in Fig. 5b (left axis). For the 327 case, the fits to the Arrhenius form were performed from room temperature to  $\sim 200$  K, as shown in Fig. 5c, where thermal activation is expected. At ambient pressure, the fit in this temperature range results in an energy gap of  $\sim 270$  meV, larger than expected for this compound. Despite of this, and in contrast to  $\text{Sr}_2\text{IrO}_4$ ,  $\Delta$  is suppressed monotonically with pressure for  $\text{Sr}_3\text{Ir}_2\text{O}_7$ , decreasing below 10 meV at the highest pressures. This evidence suggests a MIT above the 100 GPa pressure limit achieved in these experiments.

It is surprising that an increment of 40 GPa, from 62 GPa to 104 GPa, did not cause a large effect (if any) in the transport properties of the 327 compound. A possible explanation could be that pressure did increase effectively in the regions where the ruby chips were located, but not in the region of the sample located in between the voltage leads. Another less technical possibility would be to ask whether pressure beyond 100 GPa would actually be sufficient to drive the system to a metallic state. In Ref. 10, it has been shown that the introduction of very small amounts of oxygen vacancies into single crystals of  $\text{Sr}_2\text{IrO}_{4-\delta}$  led to an MIT for  $\delta \sim 0.04$ . This small amount of doping, however, increased the Ir-O-Ir bond angle  $\theta$  by less than  $1^\circ$ , far less than the previous estimation of  $\Delta\theta \sim 13^\circ$  necessary to close the  $\sim 100$  meV Mott gap.[19] This suggests that perhaps structural changes induced by pressure are insufficient to transform the system to a metallic state. It would be interesting to measure the evolution of the Ir-O-Ir bond angle at high pressures and to study its relationship with the transport properties.

In summary, we have measured the electrical resistivity of  $\text{Sr}_2\text{IrO}_4$  and  $\text{Sr}_3\text{Ir}_2\text{O}_7$  under externally applied pressures, up to 55 GPa and 104 GPa, respectively. In both cases, no signature of a pressure-induced metallic state has been found up to the maximum pressures achieved. For  $\text{Sr}_2\text{IrO}_4$ , the pressure dependence of the energy gap displays non-monotonic behavior, in contrast to previously reported results. The resistivity of  $\text{Sr}_3\text{Ir}_2\text{O}_7$ , measured at 10 K, decreases by more than five orders of magnitude between ambient pressure and 104 GPa, suggesting the proximity of this compound to a metal-insulator transition.

## E. ACKNOWLEDGMENTS

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